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ANALYTICAL CHEMISTRY

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NOTICE

ABSTRACT

Research and development were directed toward the development and improvement of standards or standard procedures for the analyses of rocket propellants. Instrumentation techniques were stressed as a means of obtaining fast, accurate and reliable analyses.

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I. SUMMARY

A major highlight of the year has been the acquisition and use of new and advanced instrumentation and accessories. This equipment has greatly increased the capability for the application of modern analytical techniques and has been of value not only in connection with analytical research but also in services rendered to other sections of the Engineering Laboratories Department and to other departments in the Aerospace Rockets and Avionics Divisions.

Some of the instruments acquired and significant applications are:

(1) Perkin-Elmer, Model 421, Grating Infrared Spectrophotometer

(a) By incorporating a high pressure gas absorption cell in the permeability test apparatus being developed under NASA Contract NAS 7-149 it has been possible to make repeated measurements of the quantity of propellant vapors (MON) permeating through teflon test specimens.

(b) Employing specialized sampling accessories, including a microbeam condenser, it was possible to identify the source of contamination which had resulted in the interruption of a gyro test program in the Avionics Division.

(c) By making use of an attenuated total reflectance unit it was possible to make a brief preliminary survey of variations in teflon and silicone rubber bladder materials.

(d) Using a ten-meter gas absorption cell, a high resolution spectrum of CO_2 gas was recorded for use in checking theoretical calculations in connection with spectroscopic combustion studies.

(2) Micro Reactor Accessory for the Perkin-Elmer Model 154D Vapor Fractometer.

(a) Measurements were made of the desorption of oxygen, nitrogen, carbon dioxide and water from carbon black thermal insulation in an induction furnace. The measurements were made as a function of time and at temperatures up to 380°C.

(3) Coleman Carbon-Hydrogen Analyzer.

(a) This instrument has made it possible to analyze synthetic solid propellants within a few hours after preparation. Previously this work was sent to an outside laboratory and at least a week elapsed before the results were available.

Research on the analysis of liquid rocket propellants with particular emphasis on increasing the accuracy and precision of results has continued.

A significant trend during 1962 has been the increasing application of analytical group capability to problems in connection with the purity, contamination, and compatibility of engineering materials. Considerable work has been done with lubricants, hydraulic fluids, solvents, and plastic materials.

II. INTRODUCTION

Research and development efforts were primarily directed toward the development and/or improvement of standard procedures for the analyses of rocket propellants. Instrumentation techniques were stressed as a means of obtaining fast, accurate and reliable analysis.

III. RESULTS & DISCUSSION

A. INFRARED METHODS OF ANALYSIS

As results of the outstanding performance and versatility of the Perkin-Elmer Model 421 Grating Infrared Spectrophotometer and its accessories (Figure 1), it has contributed strongly to the following achievements of the Analytical Group of the Chemistry Section.

In support of the activities of the Avionic Division, a contamination study on the surface of the slip ring of the gyro assembly was developed and followed up with satisfactory results. Infrared spectroscopic methods have been developed to separate and identify complex organic materials such as epoxy resins, solder flux rosins, and silicone grease. Utilization of the micro sampling accessories available with the instrument provides unlimited possibilities for analytical service to other sections in the future.

Because of the multiplicity of problems involving gaseous and vapor phase samples, no single type of gas cell is adequate for all the measurements. For trace analysis it is necessary to use a long path cell. A 10-meter multiple path cell has been assembled and calibrated.

With the double beam high resolution performance of the Model 421 Infrared Spectrophotometer, a differential technique has been adopted for the identification and semi-quantitative determination of the additive in oil.

A study of the different distillation cuts of the three-component CH_2Cl_2 - H_2O - IPA mixture has been used to evaluate the efficiency of distillation as a method of separation. The composition of each distillation cut was carefully evaluated.

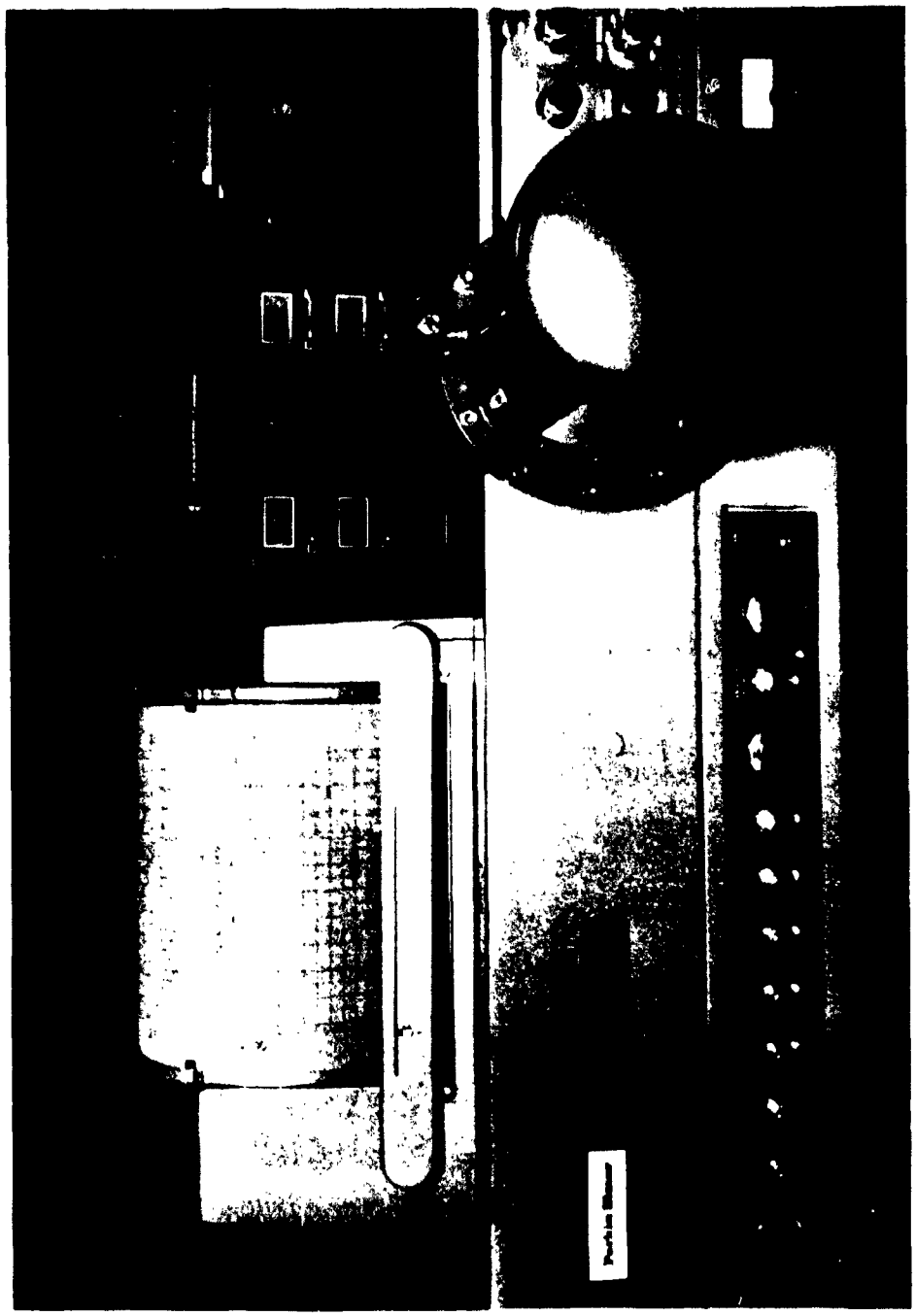

Figure 1. Perkin-Elmer Model 421 Grating Infrared Spectrophotometer and its Accessories

A new method for the production of intense and sensitive reflection spectra of strongly absorbing substances has been employed. The spectrum thus obtained shows a high degree of similarity to ordinary absorption spectra. This Attenuated Total Reflection (ATR) technique will be useful in many cases in which normal infrared techniques fail due to the difficulties in sample preparation. The special features of this ATR technique find important applications in the solid propellant project where the samples are in a spongy solid state and no solvents are available.

B. GAS CHROMATOGRAPHY

The micro reactor accessory of the Model 154D Vapor Fractometer was installed and operated satisfactorily. The techniques and applications of the micro reactor were critically evaluated. The study of the desorption of H_2O from lamp black as a function of temperature and time has proved the micro reactor to be highly useful for such types of analysis.

An initial attempt to trap the gas chromatographic effluents of the lamp black at various temperatures for further identification by infrared spectroscopy was satisfactory. More study has to be done along this line in order to increase the usage of the micro reactor in the future.

The printing integrator for the Model 154D Vapor Fractometer was installed and checked satisfactorily. A statistical evaluation program was initiated to compare the accuracy of methods of calculation by peak height, printing integrator, and planimeter. The resultant data was programmed in an IBM 704 computer and it was found that the corresponding deviation of each method was within the experimental error (see Table I).

Theoretically, the printing integrator should give the highest accuracy. After an adjustment had been made by the vendor another check was made. H_2O in the range of 0.01 to 0.04 was measured with an average deviation of ± 0.0001 cc.

TABLE I

COMPARISON OF ACTUAL DATA-H_2O CONCENTRATIONS IN 50/50 FUEL BLEND AS FOUND BY GAS CHROMATOGRAPHIC MEASUREMENTS

Actual H_2O Present %W	Integrator	Planimeter	Peak Height
0.48	0.52	0.51	0.49
	0.58	0.51	0.49
		0.52	0.50
1.01	0.93	0.99	1.02
	0.92	0.92	0.99
		0.93	0.99
1.61	1.62	1.70	1.64
	1.69	1.58	1.60
2.17	2.13	2.20	2.19
	2.11	2.14	2.16
		2.18	2.15
2.87	2.93	2.87	2.85
	2.91	2.89	2.89
		2.89	2.89
Avg. Deviation	±0.06	±0.04	±0.02

The molecular sieve V-A column for gas chromatography was found very satisfactory in separating the CO_2 - CO, O_2 and N_2 quantitatively.

C. HIGH ENERGY FUEL

50/50 UDMH and N_2H_4 Fuel Blend - A gas chromatographic field test method of water content in the 50/50 fuel blend was developed as a laboratory procedure for routine use. The direct determination of water content is perhaps the most difficult problem presented, however, the precision and accuracy of this method was found to be ±0.02 percent.

A near infrared spectrophotometric method has been adopted for the routine determination of the 50/50 UDMH and N_2H_4 content of the fuel blend. The Beckman DK-1 ratio recording spectrophotometer was employed for this work.

D. STORABLE OXIDIZERS

Allied Chemical Company's procedure for the determination of nitric oxide in MON was evaluated (Reference 1). The principle of this method was a direct oxidation of the NO in a 2 inch diameter stainless steel bomb to form N_2O_4. By the difference of the weights of the stainless steel bomb before and after the oxidation, the percent weight of NO can be calculated.

The precision of the existing melting point and titration methods and the bomb method were evaluated statistically (see Table II).

As indicated in the table, the bomb method has better precision and gives slightly higher results than the other two at the 95 percent confidence level. A routine procedure has been established in the Propellants Laboratory.

To obtain reliable analytical data for the evaluation of a permeability test apparatus, a pair of high pressure infrared gas analysis cells were procured. These cells were modified in order to improve their compatibility with rocket propellant vapors. Calibration runs were made with a series of nitrogen tetroxide/nitrogen gas mixtures up to 200 psig total pressure.

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TABLE II

EVALUATION OF NITRIC OXIDE DETERMINATION METHOD

No. of Determinations	Melting Point	Neutralization	Bomb	Bomb
n = 1	9.5	9.72	10.37	-
2	9.8	10.10	10.37	-
3	9.5	9.91	10.59	10.59
4	9.5	10.00	10.51	10.51
5	9.8	10.07	10.54	10.54
6	9.8	10.01	10.49	10.49
7	10.0	10.18	10.52	10.52
8	9.4	10.10	10.51	10.51
9	9.8	10.07	10.51	10.51
10	9.8	10.15	10.47	10.47
11	-	-	10.53	
12	-	-	10.59	
13	-	-	10.56	
V	0.039	0.018	0.005	0.0011
S	0.196	0.134	0.073	0.033
95% CL $P = \frac{TS}{\sqrt{n}}$	±.14	±.09	±0.043	±0.042
X	9.69	10.03	10.505	10.517

Data was obtained which indicated that inert pressurizing gases up to 200 psig do not significantly effect the intensity of the N_2O_4 absorption bands used for quantitative analyses.

E. COMPATIBILITY STUDIES

A study of the effect of curing on the compatibility of Knowlton 071962-A-6 teflon with various oxidizers, fuels, and solvents was undertaken. The specified curing cycle was 5 minutes at 500°F followed by 15 minutes at 600°F.

A preliminary test showed that while the teflon withstood the 500°F temperature, it was badly charred at 600°F. Therefore, the compatibility tests were run after the first curing stage. The results are given in Table III.

F. COMPATIBILITY OF 100% DACRON

The results of a seven-day compatibility test of 100% Dacron in different fluids can be summarized as follows.

The 100% Dacron disintegrated immediately on contact with oxidizers such as IRFNA, MON, N_2O_4. In the fuels, N_2H_4 and the blend, it broke up within 24 hours. No attack was visibly noticed when the 100% Dacron was contacted with the flush fluids such as methanol, isopropanol, methylene chloride, and inhibited water.

G. ANALYSIS OF SOLID PROPELLANTS

An automatic carbon-hydrogen analyzer (Figure 2) was purchased and checked out for performance, and is being used for the micro determination of carbon and hydrogen contents of solid propellants.

A remote control Schöniger Model 141R apparatus for the determination of boron was also installed and calibrated for laboratory use.

TABLE III

COMPATIBILITY TESTING

Fluids		Physical Appearance of Teflon	Physical Appearance of Fluid	Wt. Loss .gm
1. N_2H_4	Noncured	Light brown-purple (0.4728 gm Sample wt.)	N_2H_4 slightly tinted-yellowish - no residue	-0.0079
	Cured	No discoloration (0.5832 gm)	N_2H_4 discolored yellowish brown - no residue	-0.0133
2. UDMH	Noncured	Light brownish - purple (0.4132 gm)	UDMH clear	-0.0025
	Cured	No discoloration (.2273 gm)	UDMH clear	-0.0033
3. 50/50 Blend	Noncured	Light brown-purple (0.5171 gm)	Clear liquid	+0.0048
	Cured	(0.2756 gm)	Blend discolored only slightly	-0.0040
4. Methanol	Noncured	Light brown - purple (0.4744 gm)	Clear liquid	-0.0100
	Cured	No discoloration (0.2613 gm)	Clear liquid	-0.0043

TABLE III (CONT)

Fluids		Physical Appearance of Teflon	Physical Appearance of Fluid	Wt. Loss gm
5. Isopropanol	Noncured	Light brown - purple (0.4398 gm)	Clear liquid	-0.0086
	Cured	No discoloration (0.5113 gm)	Clear liquid	-0.0043
6. Methylene Chloride	Noncured	Light brown - purple (0.4063)	Clear liquid	-0.0107
	Cured	Clear (0.6082)	Clear liquid	-0.0017
7. Chromic Acid	Noncured	Light brown - purple (0.4744 gm)	Clear liquid	-0.0034
	Cured	No discoloration (0.2706)	Clear liquid	-0.0054
3. N_2O_4 (Cured Only)		Bleach coupons white (0.6115 gm)	Liquid evaporated within 24 hours leaving a thin layer of residue at bottom of beaker	0.07
9. MON (Cured Only)		Bleached coupons white (0.5509 gm)	Liquid evaporated within 24 hours heaving a thin layer of residue at the bottom of beaker	0.0583
10. IRFNA (Cured Only)		Teflon appeared to shred and loosened binder immediately	No visible change	-

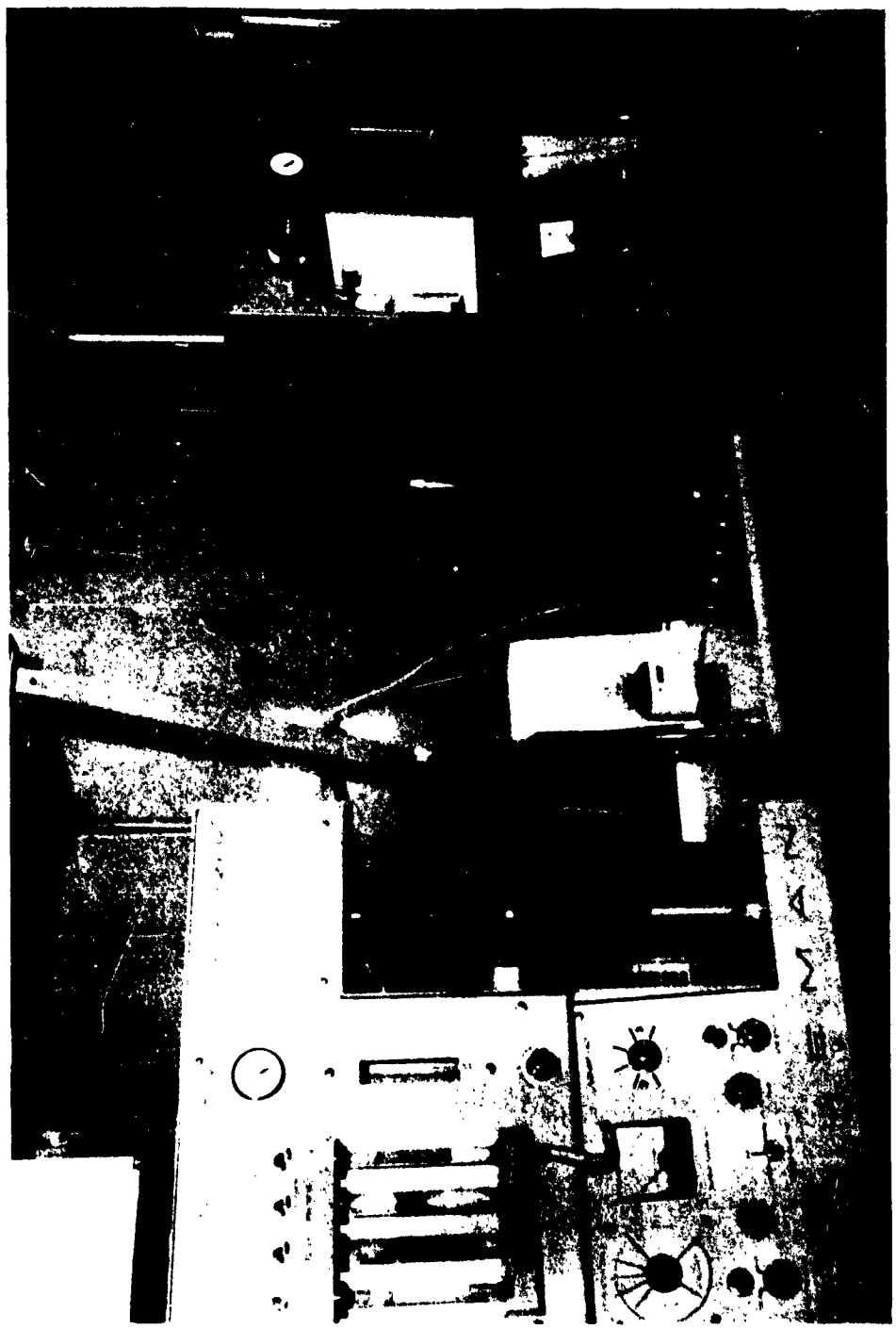

Figure 2. Coleman Carbon-Hydrogen Analyzer

By taking advantage of the variety of operating modes of the 421 Spectrophotometer it has been possible to obtain high resolution spectra of PEH. This has not previously been possible. It is believed that these spectra will make it possible to make a more complete correlation between the infrared absorption and the polymer structure.

IV. CONCLUSIONS

The availability of new, modern instrumentation and laboratory equipment has made it possible for the Analytical Group to accomplish its goal of increased accuracy, precision, and rapidity of analytical procedures. In addition, the scope of applications has been broadened to the point that the analysis of materials other than propellants has become an important phase of the operations with no significant decrease in propellant chemistry.

V. REFERENCES

1. Analytical Procedures for Mixed Oxides of Nitrogen, Allied Chemical Corporation, Hopewell, Virginia.